





# Mechanical properties of plasma polymer films: a review

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Received: 1 February 2021 / Accepted: 11 May 2021

Published online: 22 May 2021

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## Abstract

Plasma polymers are micro-, or more commonly, nano-sized coatings that can be deposited on a variety of substrates through different approaches. The versatility of these polymers is incremented by the possibility to use other precursors than conventional polymerization reactions and by potential changes in the polymerization mechanisms according to the intrinsic physical and chemical properties of the plasma. That flexibility offers a fruitful ground to a great range of scientific and engineering fields, but it also brings many challenges for universalization of empirical observations. In this review, the use of different precursors, substrates and changes in plasma external parameters were evaluated as common, but not necessarily ideal nor exhaustive, variables for the analysis of mechanical properties of plasma polymer films. The commonly reported trends are complemented with the exceptions, and a variety of hypothesis drawn by the empirical observations are shown. The techniques and methods used for determining the mechanical properties of plasma polymers, the effect of post-treatments on them and some applications are evaluated. Finally, a general conclusion highlighting the challenges of the field is provided.

## Article highlights

1. The mechanical properties of plasma polymers are evaluated as a function of selected parameters.
2. The techniques of characterization of mechanical properties of plasma polymers are summarized.
3. A discussion of future and current demands for the analysis of mechanical properties of plasma polymers is done.

**Keywords** Mechanical properties · Plasma polymers · External parameters · Precursors · Measurement techniques

## 1 Introduction

Plasma polymers can be synthesized in a great variety of structures which are often far from the ones of the precursors used [1–4]. This is explained by the random (poly) recombination of fragments and atoms occurring during the plasma polymerization process which renders the

structure of plasma thin films quite irregular [5, 6]. Besides, the retention of functional groups introduced with the precursor molecules can be very high. One of the main advantages in many applications is the possibility to deposit layers with high concentrations of a mono-functional group [7, 8]. The benefit to obtain a large variety of structures whilst controlling the density of functional groups

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contributes to a very large range of achievable properties as it is shown by the high number of works reported in the literature, and it is true that the limitations are not yet fully known. Up to now, the versatility in plasma polymer structures has led to the development of an impressive array of advanced and high-performance materials in various sectors as aircraft, automotive, textile, biomedical, to name a few [9–12]. Because the value of plasma polymers is now well-established [13], one of the most demanding requirements is durability. The plasma polymers need to be resistant to ageing, oxidation and/or shrinkage, and their mechanical properties are a key requirement for their use. Because of their unique (micro)structure, their large surface-to-volume ratio, their reduced dimensions, and the constraints caused by the substrate [14], plasma polymers have different mechanical properties from those of bulk materials [15]. Depending on the nature of the substrate, the boundary can be sharp and well-defined or broader and more diffuse leading to gradients of properties. These different scenarios offer practical advantages but can lead to significant drawbacks in some cases. This is one of the reasons why some efforts should be made on understanding the relationships between microstructure of plasma polymers and mechanical properties at different scales (micro to macro). Today, this point is one of the primary goals in all applications.

The goal of this review is to provide to the readers the state of the art on the mechanical properties of plasma polymers, justified by an increasing interest on them for specific applications. After recalling the basis in plasma polymerization, the influence of plasma parameters on mechanical properties of the polymer thin films will be discussed. Then, different techniques to quantify the mechanical properties will be presented and the effect of ageing and post-treatment will be addressed. Finally, the last section will be dedicated to applications.

## 2 Plasma state and basis in plasma polymerization

### 2.1 Plasma state

Artificial plasmas can be created in a variety of systems through the use of different [16–18]: 1. pressure conditions, from reduced to atmospheric pressures; 2. types of electromagnetic field source, as radio frequency (RF) and microwave; 3. electrode configurations, as helical coupling, bands coupling and dielectric barrier discharges and 4. reactor designs, with various geometries and materials. Within that diversity, the glow of certain plasmas names as glow discharge the best-known type of non-thermal

discharge (or low-temperature plasmas) [19]. They represent plasmas that are quasi-neutral, i.e., the number of negatively charged particles equals the number of positively charged species [20]. As described by Friedrich for low pressure plasmas [21], the electrons, generated by partial ionization of the molecules and atoms in the plasma or issued from secondary electron emissions in wall interactions, are the principal sources for transferring energy to the gas. Due to the energy conservation law, the electrons are not able to transfer efficiently their kinetic energy to heavy particles by elastic collisions. Thus, the energy either remains in the subsystem of electrons, which become heated to kinetic energies of several electron volts, or it can be transferred via inelastic collisions, which in turn can be a considerable source for excitation/dissociation reactions in the plasma [22]. In addition, heavy particles in the plasma can transfer their kinetic energies to another heavy particle with high efficiency and result in the excitation, fragmentation or ionization of the molecules. That process is favored with the increase in pressure [23]. Besides, excitation and de-excitation processes produce the electromagnetic radiation (i.e., glow) which also contributes to these reactions. In summary, a variety of different reactions may proceed at the same time, including: ion–molecule, excited species–molecule, excited species–ion, free radical–molecule, excited species–free radical, radical–radical. The rates of these processes can vary considerably and they depend on the nature of the gas and on plasma parameters such as temperature, electron densities and the number of densities of the neutrals [17]. All these may change the rates of reactions, since each type of interaction responds to changing plasma conditions in a different way.

The glow discharge at low pressure was described as an illustrative example of an artificial plasma state commonly created in plasma-enhanced vapor deposition of plasma polymers. Other discharges, as at atmospheric pressure for instance, have to consider other phenomena to the generation of non-thermal plasmas [24]. It is worth to note that the list presented in the beginning of this sub-section is non-exhaustive and other variables that affect the plasma state, and consequently the plasma polymerization, will be discussed throughout the review. The review focused on the influence of selected processing variables in the mechanical properties of plasma polymers instead of the variables related to the overall reactor design, as the ones previously listed. However, any variable that affects the physical and chemical properties of the plasma phase is important. Only through the control and understanding of the plasma phase that is possible to master the plasma polymerization and selectively direct it into a desired application.

## 2.2 Plasma polymerization

One of the most important applications of plasmas is the synthesis of (ultra)thin films in non-thermal discharges. Plasma polymerization consists in the formation of high-molecular-weight thin films from initial low-molecular-weight substances (usually named precursors or monomers) [25]. An important feature in plasma polymerization is that any unsaturated or saturated organic compound can be polymerized. This is in contrast to conventional polymerization that requires polymerizable features (such as double bonds), which are very specific in their reactivity. Also, plasma polymer thin films deposited from a non-thermal discharge are different in both chemical and physical properties when compared to polymers deposited in more conventional ways. A large number of reactions pathways are available during plasma excitation and the polymers formed in this environment are usually complex and highly crosslinked [5]. More details on plasma polymerization can be found on numerous reviews in the literature [5, 17, 26, 27].

The mechanism of deposition can be described in a simple way as follow: when a particle, which can be monomeric, oligomeric or a fragmented molecule (as ions, ion-radicals, free radicals, excited molecules or neutral species) is adsorbed onto the surface, it can react with atoms or molecules of the surface of the substrate. They can also react with each other via ionic or free-radical mechanisms and be part of the film forming process. Because the first adsorbates are anchored to the surface, they are responsible for the adherence of the growing film to the substrate. The complication arises from the fact that the newly formed adsorbed and reacted species are further subjected to the energetic components of the plasma environment, i.e., permanent bombardment with plasma particles and energy-rich UV photons. Thermal effects (local heating) can also contribute to this complexity. This is a continuing process which imposes additional changes in the newly arrived adsorbates and thus additional or changed reactions, including crosslinking, in the growing film. Finally, the final properties of the plasma polymers depend mainly on the plasma conditions as precursor flow rate, pressure, discharge power but also on other variable parameters such as the geometry of the system, the reactivity of the starting precursor, the frequency of the excitation signal and the temperature of the substrate [17]. Plasma polymers can be deposited as nanometer-thick, and sometimes micrometer-thick, layers onto all kinds of solids such as polymers, metals, powders and fibers, to name a few. The great versatility of plasma polymers brings a diversity of applications to plasma polymerization. Investigations

of the physico-chemical properties of the plasma have been explored for some time now, however only recently a greater interest on the mechanical properties of those polymers is emerging. The next session is dedicated to the evaluation of those properties in regard to the most commonly reported parameters investigated in the literature about the topic.

## 3 Plasma polymers: selected parameters that influence mechanical properties

### 3.1 Input power: a parameter for continuous wave plasma polymerization

Input power is referring here to the electrical power input (W) that is set during the continuous wave plasma polymerization process. In this review, we differentiated input power, as a variable for continuous wave plasma polymerization, from the effective power promoted in pulsed plasma polymerization, which will be covered in the next subsection. It is well-known that continuous wave or pulsed plasma polymerization result in different crosslinking and chemical composition of plasma thin films [5]. The separation of those two processes is important to highlight that the modulation of either input power or the effective power could have different impact in the final mechanical properties too. For example, it has been shown that the plasma polymerization of vinyltriethoxysilane in continuous wave plasma (50 W, 0.02 mbar) resulted in a film with a Young's modulus value between the ones obtained for pulsed plasmas with effective powers of 0.05 and 5 W, but with a peak power of 50 W [28]. The authors have calculated an effective power density ( $\text{W}/\text{cm}^3$ ) in which the value for continuous wave plasma fell in between the ones of pulsed plasma, thus explaining the observed values of elastic modulus. The fact that a significant difference is observed when input or effective power are translated to a spatial dependent variable, such as the effective power density, reflects the complexity of plasma polymerization process, which cannot be fundamentally discussed and interpreted without a thorough consideration of temporal and spatial variables, the intrinsic properties of the plasma and understanding of the polymer growth mechanisms.

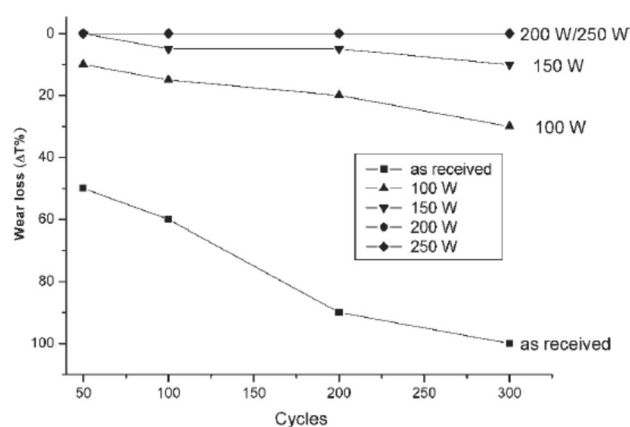
In this context, it is important to mention that composite parameters, such as the one from Yasuda [29], might be better representations of a power input parameter [30]. However, as pointed by Yasuda, even those composite parameters are still system-dependent to an extent. In addition, Yasuda's parameter has been shown to be useful for an optimization within a single system, but not able to provide the same plasma polymers in different systems [31]. In view of the intricacy of the plasma polymerization

process and the impossibility to detail the peculiarity of each literature consulted without deviating from the main goal of focusing on the mechanical properties, we have selected external parameters, as the input power and effective power, to analyze and discuss trends. That selection follows a common practice of the scientific community that is still rather phenomenological, as already addressed for other process properties [17]. Another parameter that is important to highlight is the pressure. It has a direct effect on the probability of collisions and it has been shown to be detrimental to the hardness and elastic modulus values of hydrocarbon coatings [32, 33]. However, as the effect of pressure on the mechanical properties was less frequently analyzed in the consulted literature and as it is a parameter more susceptible to variations of reactors types and feeding systems, it will not be further analyzed in the current review.

An increase on mechanical properties—i.e., hardness and elastic modulus—is commonly reported with an increase in input power. That is a result of the increase in precursor fragmentation with input power increase. As the input power scales with electron density and sheath potential, the energy flux density is consequently enhanced with its increase. The expected result from that are more crosslinked and less functionalized films. Again, it is important to note that the input power is only one of several codependent parameters to influence the final mechanical properties – as the precursor chemistry, its flow, the pressure, the substrate and reactor geometry, to name a few.

Good examples of the common trend mentioned before in which increasing input power results on higher elastic modulus can be found in literature [26, 34]. In addition, as tribological and mechanical properties are closely related, some tribology results showed to follow a similar behavior. For instance, input power effect on wear resistance has been analyzed [35]. It was investigated the effect of a thin plasma polymer layer of transparent organosilica (tetramethylsilane and oxygen as precursors) in the wear resistance of polyethylene terephthalate (PET). The deposition of the thin plasma film showed to improve the wear resistance of the substrate and an increase on input power resulted in further improve in wear resistance of the thin film (Fig. 1).

The great increase on the wear resistance was analyzed as a function of the hardness, the atomic composition and the thickness of the thin layer. In contrast, the possibility of an increase in input power resulting in lower film hardness and lower reduced modulus has also been reported [36]. The hypothesis for that observation was based on different growth mechanisms for each input power that resulted in a film in a higher stress state at lower power.



**Fig. 1** Wear loss of untreated PET substrates and organosilicon plasma polymerized coated PET substrates at various input powers as a function of wear cycles loading. Reproduced with permission [35]

To conclude, we point that the modulation of the peak power provided in a pulsed plasma polymerization might have a similar impact on mechanical properties of a plasma polymer to what has been described so far. But as the modulation of the effective power is generally done by changing the duty cycle and not the peak power, it is important to discriminate these two variables. That importance should become clearer as we discuss the influence of effective power (duty cycle) and the precursor.

### 3.2 Effective power: a parameter for pulsed plasma polymerization

Pulsed plasma polymerization is a variant in plasma polymerization frequently used. The idea is to modulate the electrical discharge on the ms-μs time scales. Thus, two distinct reaction regimes, corresponding to the “on”- and “off”- periods are generated. We can define the duty cycle (DC) as the ratio between the “on” ( $t_{on}$ ) time and the total time ( $t_{on} + t_{off}$ ) and the effective power ( $W_{eff}$ ) as the product between the peak power ( $W_p$ ) and the duty cycle. As in the equations below:

$$DC = \frac{t_{on}}{t_{on} + t_{off}} \quad (1)$$

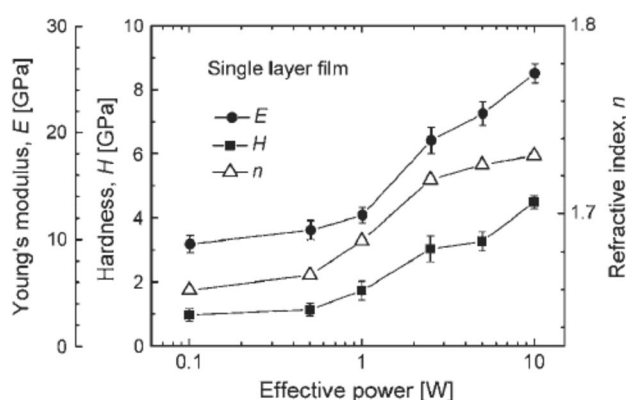
$$W_{eff} = W_p \times DC \quad (2)$$

It is expected that plasma polymerization occurs during both the “on”- and the “off”- periods while radical and ionic processes prevail during the “off”-period. During the “on”-period, the precursor fragmentation and substrate activation take place. A gas-phase polymerization is initiated during the off period by the species previously



generated. At that stage, the plasma does not disturb the polymerization process and thus is not able to introduce defects [21]. Such pulsed plasma, with long plasma “off”-periods and short “on”-period pulses, offers a good compromise for efficient production of polymer structures with a minimum of irregularities. The duty cycle and the repetition frequency of pulses plays an important role. The use of a low duty cycle and a low peak power allow to minimize the crosslinking and maximize the retention of functional groups and, thus, one dominant sort of functional group should be formed [5, 7]. However, it is now well-accepted that retention of complete structure elements of precursors is quasi-impossible. To conclude, using the pulsed mode, the plasma polymer should consist of more chemically regular products than those of the continuous mode. These differences in term of polymerization mechanisms can be used to control variations of chemical compositions and physical properties of the material surfaces.

Similarly to the trend observed with input power, the most commonly reported result of an increase in effective power or duty cycle is an increase in Young's modulus or/and hardness. For instance, Cech et al. [37] changed effective power (0.1–10 W, 1.3 Pa) to produce different single and multi-layer plasma thin films of tetravinylsilane. Mechanical properties of the single layer films increased with increasing effective power (Fig. 2). Likewise, Veuillet et al. [38] observed an increase in the Young's modulus when the effective power was increased for plasma thin films of 2-hydroxymethyl methacrylate (HEMA), even if the chemical composition of the films has not differed considerably. The authors also determined the Young's modulus of plasma thin films of dimethylaminoethyl methacrylate, but in the range of effective power studied no significant difference of the mechanical properties were observed.



**Fig. 2** Young's modulus, hardness and refractive index of a single layer of plasma thin films of tetravinylsilane. Reproduced with permission [37]

### 3.3 Nature and ratio of precursors

The current work focused on reviewing the mechanical properties of plasma-polymerized thin films from organic precursors. Due to relatively scarce literature on that subject, organosilicons, that can produce plasma polymers with a more organic or inorganic character, were also included. They are undoubtedly the ones in which those properties are more frequently analyzed, probably because many applications to which they are explored directly demand that investigation. Some of those applications will be detailed later in this review. As previously reported [27], the mechanical properties are one of the least explored characteristics of functionalized plasma depositions. However, as the interest in exploring other possible applications grows [9], the investigation of those properties for other organic precursors than organosilicons is also increasing.

The structure and chemistry of precursors are important variables for tailoring the mechanical properties of plasma thin films and should be carefully taken into consideration for that. The presence or absence of saturation, for instance, defines the dominant mechanism of film growth—ionic or neutral—and consequently impacts the crosslinking and elastic modulus of the plasma polymerized film [26]. The effect of crosslinking degree on the mechanical properties of polymeric materials is widely reported and it has been also directly demonstrated for plasma polymerized thin films [39]. Precursor selection is fundamental for determining how other parameters for deposition should be tuned. For example, propanethiol-based plasma polymers showed similar crosslinking degree with effective power increase, when the power was modulated by the “off-time” [40]. In contrast, crosslinking degree of allylamine and ethyl lactate-based plasma polymers increased when the same parameter was changed [41]. Those differences were justified by the different growth mechanisms of each polymer, which are intrinsically associated with the structure and chemistry of the precursor.

Different precursors can also be plasma polymerized together. The evaluation of the mechanical properties of films from such copolymerization is more reported for mixtures of organosilicons and hydrocarbons [42–45]. As expected, that kind of approach does not seem to result in films with completely different mechanical properties from the single monomeric films, but rather in-between them. For instance, the mixture of hexamethyldisilane with xylene promoted intermediate mechanical properties to those of the films based only on one precursor [44]. In terms of the interdependence of copolymerization and another polymerization parameter, such as deposition power, Lee et al. [43] showed that hexamethyldisiloxane

and 3,3-dimethyl-1-butene plasma thin films had their hardness and elastic modulus increased with higher plasma deposition power. That is a similar trend to what could be expected for those single precursors, even if from distinct growth mechanisms.

The possibility of plasma polymerization of organosilicons and oxygen has been also reported. In these systems, oxygen has fundamentally the roles of a “crosslinking agent” and “functionalizing agent”—which is related to its potential to shift a deposition process to etching. The duality of those roles has a great impact on the mechanical properties outcome. They are dependent on the fraction of oxygen and on the other plasma deposition parameters [46]. For instance, the use of higher input power and higher oxygen ratio, for plasma polymerization deposition of hexamethyldisiloxane and oxygen, generated films with high tensile stress or even provoked spontaneous cracking (Fig. 3) [47].

In regard to its role on the polymerization of tetravinylsilane [48], oxygen was shown to promote the formation of stronger chemical species (Si–O–C) at lower power (0.1 W, 1.4 Pa), resulting in a small increase in the Young's modulus. The same system at higher power (2.5 W, 1.4 Pa) had, however, a more organic nature and oxygen was also incorporated as carbonyl and hydroxyl functionalities. In that case, the insertion of the functionalities implies a reduction on the possible crosslinking of the carbon atoms, resulting in decreased mechanical properties. A recent work has demonstrated the correlation between mechanical and optical properties of these thin films [49]. Zhang et al. [50] verified the influence of changing power on the interface roughness of multilayered plasma thin films of hexamethyldisiloxane. The authors analyzed the interface roughness of a multilayer film made by “harder

layers”, produced with higher power and oxygen flow, and “softer layers”, produced with lower power and without oxygen. The interface roughness was around 10 nm when the “harder layer” was deposited on top of the “softer” one and only of 3 nm in the reverse case. That result was attributed to partial etching of the film by the subsequent deposition process. The authors also observed the differences in mechanical properties of each layer via force displacement curves obtained by nanoindentation measurements. Similarly to what was reported with oxygen, hydrogen has also been used as an etching gas [32] and water has been used to oxidize organosilicons. For the latter, the mechanical properties were increased by the formation of a Si–O–Si network [51] and the chemical and mechanical properties were analyzed after annealing the films [51, 52].

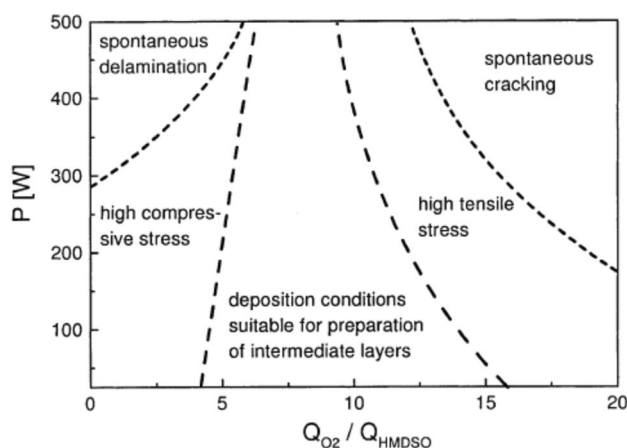
Although they cannot be considered precursors, rather more like “catalysts” and “dopants”, noble gases are able to promote differences in the final mechanical properties of plasma thin films [53]. For instance, when the proportion of argon was increased in regard to hexamethyldisilazane the hardness of the films grew monotonically [54]. That result was explained by a more effective bombardment of the precursor, which promoted higher crosslinking. The authors also point to a possible effect of ion implantation on the films structure. An increase in hardness was also observed for the deposition of another organosilicon with argon, when compared to the deposition of the same precursor with water [51].

Similarly to other polymerization process, nature of the precursor (or monomer) is one of the most critical factors determining the final properties observed in plasma polymers. Furthermore, the peculiarities of plasma polymerization allow the use of broad range of precursors and, as it essentially comprises a phase transition, other factors have to be considered. In that sense, the substrate is quite an important one as it is where the polymer formation starts.

### 3.4 Nature of substrate

One of the most commonly reported advantages of the use of plasma polymerization deposition process is the fact that it can be performed in a wide range of substrates. That great versatility is proved by the variety of substrates already explored, as polymers (thermosets and thermoplastics), silicon wafers, glasses and metals for example. As an important variable on plasma polymerization procedures, the reports on substrates influence on mechanical properties of plasma polymerized thin films will be briefly discussed.

As a technical limitation, a possible effect of the substrate in the measurement of mechanical properties of thin films is widely accepted and that aspect will be covered in the next session of this review. In addition, a



**Fig. 3** Schematic representation of mechanical properties dependence on the power as a function of the ratio between oxygen and organosilicon. Reproduced with permission [47]

long-established influence of the substrate on how plasma polymers bonds to its surface should be acknowledged [55]. The mechanical properties of a generated interface/interphase between substrate and plasma polymer is of great importance for many applications, as they could be detrimental to type of failure observed when the final material is mechanically solicited. Furthermore, that interface/interphase might be also pertinent for a prospective mechanical analysis of ultrathin plasma films. The influence of the substrate on the rate of deposition and chemistry of ultrathin films is known for some time [56] and a recent publication reports how the chemistry of the substrate creates different morphologies of plasma thin films during early stages of growth [57]. Those latter results open up for questions on the possibility to measure localized mechanical properties within plasma polymerized thin films. Of course the feasibility of such analysis depends on overcoming technological issues, as in that scale even the Van der Waals forces from the substrate are shown to play a role on interfacial interactions of ultrathin plasma polymerized films [58].

There are a few reports on the effect of changes in the substrate on selected mechanical and tribological properties of plasma polymerized thin films. For instance, it has been observed that a plasma pre-treatment of an elastomer impacted on the coefficient of friction and wear rate of an organosilicon-based plasma polymerized coating [59]. A decrease in roughness of the substrate after the plasma pre-treatment was associated with the observed reduction in those values when compared to the sample without pre-treatment. The explanation given was that wear resistance is improved in smoother surfaces. It is necessary to point, however, that a decrease in roughness with oxygen plasma treatment is not always observed, with the opposite behavior being reported elsewhere for a different system and substrate [60]. The temperature of a poly(ethyleneterephthalate) substrate was varied for a Townsend discharge plasma deposition of an organosilicon and the critical load assessed through scratch test. An increase on the critical load with temperature was correlated to a decrease in heterogeneity of the coating and, therefore, intrinsic stress [61].

The possibility of the substrate affecting the intensive mechanical properties, as the elastic modulus or hardness for instance, of plasma polymerized thin films has to be more systematically studied. However, its implementation might be challenging since differentiating what could be a gradient of properties within the thin film and a plausible influence of the substrate on the measurement is not simply done. A critical interpretation of the data and selection of the technique is fundamental for that.

## 4 Measurement techniques

The characterization of the mechanical properties of plasma polymerized thin films is often performed by nanoindentation. The most commonly reported approach uses a nanoindenter equipped with a Berkovich indenter. Loading the indenter promotes both elastic and plastic deformation on the thin film and unloading mainly results in the recovery of the elastic deformation [62]. The data treatment for the calculation of elastic modulus and hardness is often based on the method from Oliver and Pharr [63] from the load–displacement curves.

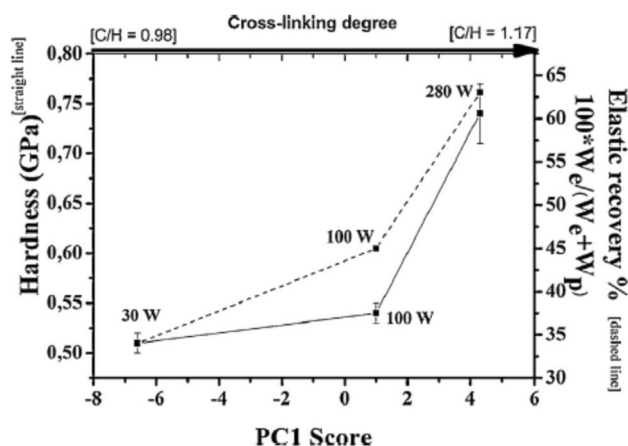
In the case of thin films, nanoindentation measurements have to take into account the possible influence of the substrate on the measured mechanical properties. To overcome that issue, it is common in literature to utilize a threshold of 10% of the film thickness as the limit for the indentation depth, known as 10% rule. However, the generalization of the 10% rule for the determination of mechanical properties in thin films can be problematic [64]. The values obtained in the analysis could still be influenced by the substrate, depending on the thin film thickness, on the difference in mechanical properties between the film and the substrate and even on the mechanical properties of the films [65–67]. Cech et al. [62] evaluated the mechanical properties of plasma-polymerized organosilicons via different nanoindentation approaches (conventional, continuous oscillatory loading, cyclic and continuous mechanical mapping). The authors have made a detailed analysis on the influence of each approach on the reported values of elastic modulus or hardness. They advocate the use of depth profiles of those properties as a standard practice, in order to verify the influence of the substrate. They also propose a list of necessary conditions for successful analysis of mechanical properties at shallow depths. Conventional and alternative nanoindentation techniques have also been evaluated elsewhere [68].

Nanoindentation can also be performed by atomic force microscopy (AFM). The mechanical properties can be quantitatively assessed through the determination of the elastic modulus [69]. In the case of AFM nanoindentation, more variation of the indenter geometry (AFM tip) is reported in literature. That results on the use of different mathematical methods for the determination of the elastic modulus of the plasma thin films. When parabolic indenters are used, the theoretical approach for the determination of Young's modulus is based on Hertz theory [26, 70]. For the case of other geometries, Sneddon's model [71] and Oliver-Pharr model [69] are reported. The use of PeakForce Quantitative Nanomechanical Mapping (PF-QNM®, Bruker) [38] and nanoDMA [72, 73] have been also

reported. The latter allows the determination of the storage and loss moduli and consequently of loss factor.

More recently, Toda et al. [34] measured the Young's modulus of plasma polymerized allylamine films through micromechanical cantilever sensor and laser-based surface acoustic wave techniques. The authors observed that smaller Young's modulus values were obtained with surface acoustic waves technique when compared to the micromechanical cantilever sensor. Those differences were attributed to either a different swelling or lower crosslinking of the films at the air interface, in contrast to the substrate interface. As one technique is more influenced by the polymer-air interface and the driving force to the other is at the polymer-substrate interface, those differences could be detected. According to the authors, one of the major outcome of the work is that both techniques could be used for the determination of mechanical properties of "ultra-thin" plasma polymers ( $\sim 100$  nm was tested).

Some other approaches can be useful for a less fundamental evaluation of plasma polymers mechanical resistance. One technique reported in literature for the determination of thin films hardness is the pencil hardness test [35, 74–77]. The pencil hardness test is commonly used to determine the hardness of organic coatings relatively to the one of a pencil lead [78]. Similarly, it is also possible to test the scratch resistance of plasma thin films, method known as nanoscratching [61, 69, 79–81]. The critical load is selected as a parameter to represent the scratch resistance and it is determined when an "abrupt" or "brittle" damage on the thin polymer is observed. The subsequent analysis of the scratch residual track can be done by optical or scanning electron microscopic analysis and provide information about the type of deformation (delamination, buckling, cracking). Some tribological tests are used to determine the wear rate and friction coefficient of plasma thin films [59, 82]. Atomic force microscopy was also used in contact mode as a way to induce wear of thin plasma polymerized hexane films and thus provide qualitative or semi-quantitative assessment of their mechanical properties [15, 83, 84]. It was observed that the extent of the wear is strongly dependent on the scanning parameters, as for example the number of scan lines. Semi-quantitative information could be extracted through the measurement of surface roughness or by the observation of the load necessary to promote a topography change of a scanned area when compared to its surroundings, coined by the authors as critical load. The possibility to assess the crosslinking degree from ToF–SIMS combined with principle component analysis has been demonstrated by Cossement et al. [41]. The authors observed a good agreement between the calculated crosslinking degree and the mechanical properties of the thin films (Fig. 4).



**Fig. 4** Hardness (straight line) and elastic recovery (dashed line) correlation to crosslinking degree determined through ToF–SIMS and principal component analysis. Reproduced with permission [41]

The diverse number of techniques and mathematical approaches exemplifies well the challenges on the determination of mechanical properties of plasma polymer thin films. The selection of a technique is directly associated with the level of information desired and the knowledge of its limitation is essential for that choice. In recent years, there is an increasing acknowledgement and determination of the variation of the plasma thin film properties on the interfaces/interphases (i.e., plasma/air, plasma polymer/substrate, etc.) and an interest in separating those influences from the plasma polymer bulk. Those fundamental aspects have been commonly explored via nanoindentation, but other techniques are having their potential starting to be explored. For less fundamental approaches, however, other methods as nanowear, nanoscratch and the pencil hardness test might fit a specific goal of a study.

The variety of techniques, by itself, complicates the comparison of absolute values of mechanical properties from plasma polymers deposited in different systems. The basic descriptions to accompany any characterization of mechanical properties of thin films (i.e., thickness, environmental conditions, measurement conditions, etc.) are important, but not always they are all presented in the literature. For conventional techniques, as nanoindentation, the state of art on the evaluation of mechanical properties of thin films is already reviewed elsewhere [85, 86] and, from the authors point of view, the much smaller scientific community of functionalized plasma polymers would benefit from a concerted effort for systematic fundamental studies of those properties. Beyond the conventional techniques, there is a lot of space for development and innovation still available in the area. The next sessions, in

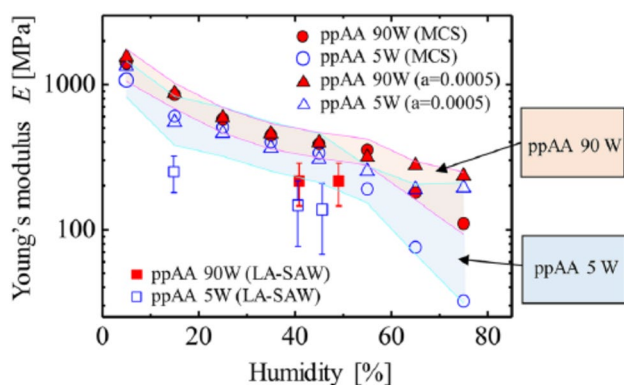


which post-treatments and some application are evaluated, might also highlight some unexplored fields.

## 5 Ageing and post-treatments

A complete transition of any plasma-polymerized thin film from the scientific research to a final application might need to take into account, at one point, aspects of stability and ageing of those films. The effect of ageing was investigated for plasma thin polymers in terms of their chemical and optical properties [87]. The chemical changes in organosilicon/oxygen promoted by ageing has been also studied [88]. To the best of our knowledge, only that latter study evaluated aged plasma thin films mechanical properties. The authors observed trends in aged films that could be explained by the changes in the deposition conditions; however, no comparison between the mechanical properties of films before and after ageing was performed. The same work group also reported the influence of post-deposition film oxidation on the hardness, which decreased with the contact depth [28]. The lack of studies on the mechanical properties of aged functionalized plasma polymers reveals a relevant gap, as mechanical properties and coating stability might be affected from that. For instance, the possibility of dangling ends on poly(acrylic acid) plasma polymers acting as internal plasticizers on the films has been demonstrated [89]. According to the reactivity of those, time-dependent post plasma chemical reactions might occur, with an expected effect on the crosslinking of the films.

In a similar way to bulk materials, if the plasma thin films are supposed to be used in a different environment, aqueous medium for example, their mechanical properties should also be tested in that condition. For instance,



**Fig. 5** Young's modulus as a function of humidity for different input powers (blue or red) and from different techniques or parameters (geometric symbols). ppAA stands for plasma polymerized allylamine. Reproduced with permission [34]

the Young's modulus of plasma-polymerized thin films have also been evaluated in phosphate-buffered saline solutions [38, 90] and the influence of humidity on the mechanical properties of plasma thin films has been also assessed [34]. A clear decrease on the elastic modulus was observed with increasing humidity (Fig. 5), regardless of technique used for the modulus calculation or power applied. That decrease could be attributed to a reduction in the molecular chain density of the polymeric network upon swelling. Films produced at lower power, however, presented a higher variation on values with humidity change than those produced at higher power. That result can be correlated to an expected lower crosslinking degree of the films at lower powers.

Although ageing is an inevitable and not easily controllable process, a material can also have its mechanical properties deliberately modified by the action of post-treatments. A common way of changing the properties of polymeric materials is through annealing. It has been shown that annealing plasma-polymerized thin films have an influence in its mechanical properties, with the most common behavior reported being a decrease in mechanical properties [44, 91]. For example, the effect of annealing temperature was investigated for p-xylene and/or hexamethyldisilane plasma polymer thin films [44]. For either the films based on a single precursor or their mixture, annealing resulted in a loss of mechanical properties, attributed to graphitization.

Nevertheless, that is not a universal behavior once other variables, as the annealing temperature and the precursor, might inflict in a different outcome. For instance, Burkey and Gleason [51] evaluated the influence of the duty cycle on the deposition of an organosilicon/water mixture and checked the effect of annealing the films (400 °C). Higher duty cycles resulted in an increase in the hardness values, which was corroborated by the increase in crosslinking verified in their FTIR results. Although in a limited scale, annealing those films resulted in further increase in their hardness and decrease in elastic modulus. That result suggests that annealing the films have an effect of promoting more crosslinking. However, when the same authors studied the influence of annealing for other four different organosilicons, also oxidized with water, the improvement of hardness with annealing was only observed in one sample [52]. That result was explained in terms of the different chemistry of each precursor and the power used for the polymerization, that resulted in favored conditions, or not, for condensation reactions to occur with annealing.

A post-treatment procedure intended to increase the silica-like character (mineralization) of an organosilicon-based thin plasma polymer film has been studied [92, 93].

In these works, the use of oxygen plasma as a post-modification of thin films was analyzed. For plasma polymerized hexamethyldisiloxane thin films [92], the oxygen plasma surface treatment promoted a slight increase in the value of hardness and maintained the elastic recovery of the films. That result was attributed to the surface treatment being effective in a limited thickness of the polymeric matrix. It is interesting to note that contact angle values significantly changed after the treatment, from 108.2° in the untreated sample to 29.4° in the treated one, suggesting a strong modification of the film composition in the surface. In the case of plasma polymerized dimethylsiloxane thin films [93], air plasma post-treatment also resulted in higher values of hardness (Fig. 6).

The authors, however, point the technical limitation they had for the measurements, as the indenter penetrates the sample much deeper and go into the soft polycarbonate substrate. They also performed scratch tests, but no difference between the mineralized and not mineralized samples was observed. The explanation given was that the polymer matrix was already highly crosslinked and not substantially affected by the low energy ion bombardment of the post-treatment.

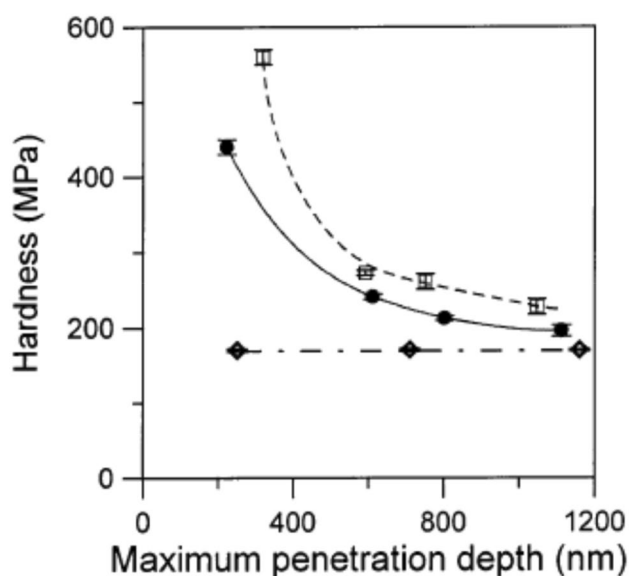
Possible post-treatments of organic plasma polymers that could be still investigated might involve thermal curing, light-UV induced reactions and post-functionalization for example. However, to the best of our knowledge, there is not any report on the measurement of the mechanical properties of plasma polymers for these processes. These

gaps of knowledge identified might be in the near future fulfilled, as the interest in new applications of plasma polymers increases.

## 6 Applications

A possible application of plasma polymer thin films is on the development of hard coatings. Several advantages of the use of plasma polymerization for that can be numbered, as it generally results in thin and uniform coatings for example. The application of a plasma polymer coating containing inorganic SiOx has been shown to improve the hardness of a polymeric substrate [75]. The use of organic precursors can also lead to plasma polymers with a broad range of mechanical properties and with potential for hard coatings application. Beake et al. [94] have showed that plasma polymerized hexane films presented greater values of stiffness and hardness than conventional polymers, as for example highly crystalline biaxially oriented poly(ethylene terephthalate) (PET). The reduced modulus of one of their coatings was almost five times higher than the one of PET. Similarly, the plasma films presented better creep resistance than conventional thermoplastic polymers, such as PET and PEO. According to the deposition parameters it was possible to even obtain creep resistance close to the one of fused silica. Besides hard coatings, organosilicon-based plasma polymers have shown to be effective gas barriers; however better barrier properties were obtained at the cost of reduced mechanical properties [95].

Another possible application of plasma polymers is as an interlayer for composite materials. This system has been investigated for the adhesion of glass fibers and polyester matrixes with the successful improvement on the composites short-beam strength reported [96, 97]. In terms of mechanical properties of the thin plasma film, one of the goals of such system is to create an intermediary layer where a transition of those properties for each constituent material is offered. As analyzed by Cech [96], if the difference in mechanical properties of the fiber and matrix is too great, there will be a high stress concentration on the fiber/matrix interface which will influence the overall performance of the composite. An interlayer with intermediary properties is able to provide some improvement, as long as its Young's modulus value is optimized for the specific system. More ideally, an interlayer with a gradient of mechanical properties would avoid any mismatching issues. Probably pursuing that goal, the same workgroup has studied the gradient properties within plasma thin films [98]. Their results from depth profiles of Young's modulus allowed to propose that the film structure comprised an interlayer at the substrate, a bulk film

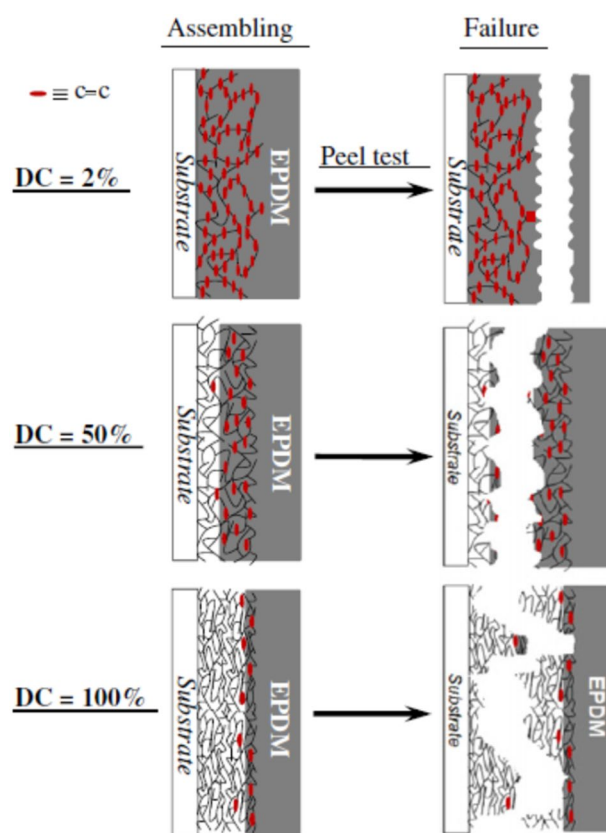


**Fig. 6** Hardness versus maximum penetration depth for polycarbonate substrate (dash-dot line), polycarbonate treated in air plasma (solid line) and polycarbonate coated with an organosilicon plasma polymer followed by air plasma treatment. Reproduced with permission [93]

and a gradient overlayer at the surface. In another work, they report the values of hardness as “bulk” and “max”, with the former calculated as a mean value of data below 20 nm thickness from the film surface and the latter at the surface [28]. When evaluating the influence of thickness on the modulus, the authors observed a decrease in that value with increasing thickness. That was attributed to a lower material compaction on the upper part of thicker films due to a slower kinetics (deposition versus ablation). In further studies [37], they deposited single and multilayered films, in which each layer was produced with one of two different powers. With the assistance of an ultramicrotome, they were able to perform nanoindentation on a 10 layers stacked film. The different layers of the multilayered film presented similar properties to the equivalent single thin film. More recently, Hoferek et al. [99] reported the formation of multilayers and linear gradient thin films for potential application in hybrid materials.

There is also potential application of plasma polymer thin films in the automotive industry, where for example the reduction in friction between two parts can benefit user comfort and product durability. An indirect assessment of the mechanical properties can be achieved by some tribological tests as the determination of the friction coefficient [100, 101]. Múgica-Vidal et al. modified glass substrates via atmospheric-pressure plasma polymerization of aminopropyltriethoxysilane (APTES). A significant reduction on the friction coefficient was achieved for thicker coatings with a more inorganic character. The authors also pointed out to the possible application of their coating in solar panels, which could also be a potential application for more organic plasma thin films. In that direction, Jabob et al. [102, 103] explored the possibility of using plasma thin films in flexible electronics. The goal was to develop an insulating material to be incorporated in organic field effect transistors. The changes in friction coefficient (nanoscratch) and Young's modulus were verified as function of deposition power, with the Young's modulus increasing as power was increased [102].

A growing interest is being directed on bringing plasma polymers closer to biomedical applications, which is well-reviewed elsewhere [9, 104–106]. In that direction, cell adhesion has been tested in regard to the mechanical properties of a weak polyelectrolyte multilayer system coated, or not, with plasma polymer thin films [90]. Coated samples presented uniform wettability and surface chemistry. The results showed that cell adhesion was favored in stiffer surfaces ( $\sim 120$  MPa) when compared to softer ones ( $\sim 0.5$  MPa). In recent works, plasma thin films with antibiofouling and antibacterial properties were shown to present excellent scratch and delamination resistance with polymer-like viscoelastic character [72, 73].



**Scheme 1** Schematic illustration of adhesive failures between aluminum substrate coated with plasma polymer and an elastomer for different duty cycles (DC). Reproduced with permission [107]

The applications listed so far are the ones in which the mechanical properties of plasma polymers were directly assessed. However, they are not an exhaustive list and in many other applications those properties could be very informative about a system. For instance, we can examine the potential use of plasma polymers as adhesives. Airoudj et al. [107] showed the influence of duty cycle on adhesive bonding between a plasma polymerized coated aluminum and a polymer. The authors observed different loci of failure according to the duty cycle used and that was correlated to the efficiency of a vapor phase post-functionalization of the plasma polymer (Scheme 1). That efficiency is directly linked with the chemistry of the polymer and its crosslinking, which almost certainly impacts its mechanical properties. In that specific case, the knowledge of the mechanical properties could thus bring more information about an expected transition from a more viscoelastic to more brittle polymer plasma with the increase in duty cycle and provide further insight on the different adhesive failures observed.

The latter example is brought to point that in some publications the mechanical properties of a plasma polymer

coating might have played a significant role to a desired application or could have been indirectly predicted—generally through an analysis of crosslinking from the films chemistry [108–110]. Even though the current review focused on the literature in which the mechanical properties of the plasma polymers were measured, we would like to credit those other situations. The advantages of plasma polymerization process, as the possibility of deposition in different substrates, the diversity of precursors and control of the reticulation allow its application to a broad range of fields. In many of them, the importance of the mechanical properties should not be underestimated and the increasing interest on that topic reveals a growing agreement on that by the research community.

## 7 Conclusion

The mechanical properties of plasma polymers thin films still remain to be largely explored, especially for functionalized organic coatings. Some efforts have focused on the possible ways to adequately characterize them and a number of techniques and approaches have been reported. One of the issues, that could be easier to address by the scientific community interested on the topic, might be a more uniform approach on characterization of those properties, as that basically requires a concerted effort and possibly standardization. A more complex issue to solve might be the well-known and previously discussed non-uniformity on the parametrization of the deposition conditions for different systems, that strongly affects the polymer being formed. However, a careful description of the characterization techniques and methods used in the determination of the mechanical properties combined with spectroscopic information of the plasma phase and plasma polymers can allow consolidation of those data over time. The peculiarity of each system cannot be generalized, but the ever-growing acknowledgement of the relation between fundamental aspects and final properties of the polymers is necessary for deepening the shared scientific knowledge on mechanical properties of plasma polymers. A thorough knowledge of the mechanical properties of plasma polymer thin films is a requirement for the future applications of those coatings.

**Conflict of interest** The authors declare that they have no competing interests.

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